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Base Exchange Studies on the Pennsylvania Jordan Field Plots

A THESIS

**PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL
OF CORNELL UNIVERSITY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY**

BY

FREDERICK G. MERKLE

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BASE EXCHANGE STUDIES ON THE PENNSYLVANIA JORDAN FIELD PLOTS¹

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The field experiments of many experiment stations, notably Rothamsted, Woburn, Rhode Island, Pennsylvania, Ohio, Massachusetts, and New Jersey, are replete with examples of secondary or after effects of the long continued use of certain fertilizers upon the soil. These secondary effects of a fertilizer may be beneficial or detrimental and may manifest themselves in many different ways. The specific feature to be considered here is the possible effect upon the relative amounts of the various exchangeable cations held by the soil colloidal matter.

Numerous workers (3, 4, 7, 17, 18, 19, 21, 23, 30, 31, 33, 35, 36, 40, 41, 42, 43, 44, 45, 46, 47, 48, 52, 53, 54) have reported direct or indirect evidence that the long continued use of a given fertilizer on the same plot of soil brings about an alteration in the relative amounts of the various so-called replaceable ions. For the sake of brevity their findings will not be discussed here.

EXPERIMENTAL

The purpose, plan, and results of this field experiment are set forth in a series of reports and bulletins (39), therefore only a brief outline will be given here. Four tiers, of 36 plots each accommodate the rotation, which consists of corn, oats, wheat, timothy and clover. Corresponding plots in each tier are fertilized alike. The fertilizers are applied to the corn and wheat, as given in the summary table appended. In the original plan only three plots in each tier received lime—either alone or with manure. Manure and 2 tons burnt lime are applied to corn only on plot 22, and 2 tons burnt lime alone, on plot 23. Plot 34 receives 2 tons of ground limestone on the corn and wheat.

In 1921, 40 years after the experiment was started, it was decided to lime tiers 2 and 4 according to the individual requirement of each plot. Tier 1 and 3 remained unlimed with the exception of those plots previously mentioned.

Nearly all plots of tier 1, which perhaps is the most uniform in soil characters, were sampled in 1927, others in 1931, and still others in 1932. It became

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² This investigation was carried out under the direction of Dr. J. A. Bizzell. The author takes this opportunity to express his appreciation and gratitude for the help extended during the prosecution of this work and for reviewing the manuscript.

apparent that plots 1 to 7 in tier 1 lacked uniformity; therefore, in 1932 plots 1, 2, 3, 4, and 8 in tier 3, also unlimed, were sampled and were found to be very homogenous. It was assumed that the liming of tiers 2 and 4 would mask the chief effects of fertilizers as it did at Rothamstead and at Ohio. Therefore, only four plots in tier 2, the ones most acid before liming, were sampled. Since yields had indicated that liming had completely restored the fertility on these acid plots, it was decided to see whether there was any fundamental difference in the exchange base content other than calcium.

The composite sample from each plot consisted of 12 borings equally distributed over the area. These were air dried, passed through a 1 mm. sieve, and stored in covered containers. For the determination of exchange base content 50 or 100 gm. of this air-dry soil were treated with 1 liter of neutral ammonium acetate. The advantages of this reagent for base exchange work have been clearly brought out by Schollenberger (46, 48).

Instead of the percolation method as outlined by Schollenberger the soil was shaken with successive small portions of ammonium acetate, allowed to settle, and the supernatant clear liquid poured on a filter. Finally the entire sample was transferred to the filter and leached with more reagent. Tests for calcium and pH showed that removal of these ions was complete.

Exchangeable hydrogen was, at first, determined by titrating the ammonium acetate filtrate potentiometrically with 0.1 *N* NH_4OH to pH 7.00. This method was used on about two-thirds of the samples. The results obtained by this method seemed high in many cases. Several soils which were definitely alkaline contained considerable exchange H by this method.

As the work progressed the advantage of direct titration seemed apparent (7, 10, 14, 15, 22, 44, 49). It was tried and the following procedure adopted. Five 5-gm. samples of soil were placed in small vials (25 x 80 mm.). To a total volume of 10 ml. of liquid, 0, 2, 4, 6, or 8 m.e. of $\text{Ba}(\text{OH})_2$ per 100 gm. of soil were added. The contents were very thoroughly stirred with a rod; then the vials were stoppered and allowed 72 hours to come to equilibrium. The hydrogen-ion concentration of the contents of each vial was determined potentiometrically. The H-ion concentrations were plotted against base added, and, from the curve obtained, the base required to bring the soil to pH 7 was determined. This was taken as the exchangeable hydrogen. The question arose whether one should use pH 7 or some higher value, pH 8 or 8.5, as the equilibrium value.

If the potentiometric and conductometric titrations of the Putnam clay sol of Bayer (8) are examined it is apparent the reaction between the H-sol and the base is not instantaneous. To neutralize his H-sol immediately, 57 m.e. of base were required whereas after 3 months 60 or 62 m.e. apparently were required. When hydroxides of lithium, sodium, potassium, calcium, and magnesium were added to equal quantities of sol at the rate of 57 m.e. per 100 gm. colloid, he obtained values below pH 7.00 in all cases, the lithium and sodium producing pH values close to 7.00, whereas potassium, calcium, and magnesium

gave the values 6.50, 5.95, and 6.19 respectively. If he had used 60 or 62 m.e. as the total exchange capacity per 100 gm. of colloid and allowed a longer time for the establishment of equilibrium, he would doubtless have obtained values above 7.00 for the lithium and sodium clays but very little above 7.00 for calcium and magnesium clay. Aarnio (1) produced single base clays by leaching with chlorides and found them to have the following pH values when all excess chloride was removed: Li 7.43, Na 7.20, K 7.02, Rb 6.60, Ca 7.77,

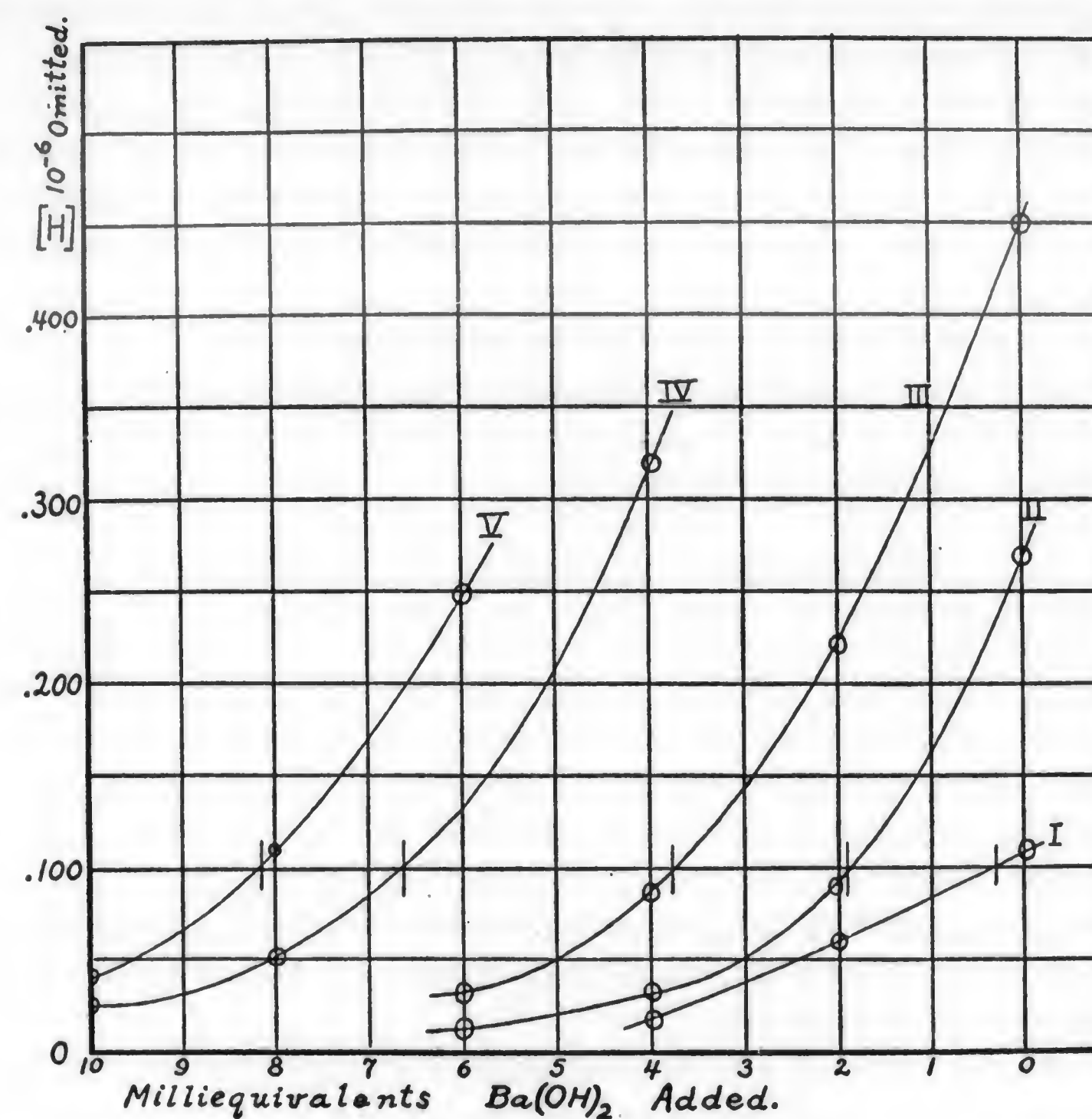


FIG. 1. TYPICAL TITRATION CURVES

- I. Plot 5, 0.30 m.e. exchange H
- II. Plot 14, 1.90 m.e. exchange H
- III. Plot 15, 3.75 m.e. exchange H
- IV. Plot 30, 6.60 m.e. exchange H
- V. Plot 31, 8.10 m.e. exchange H

Mg 7.22, Ba 7.15. When a pure H-sol is titrated with base there is generally a break in the curve at neutralization, but when a natural soil containing bases as well as hydrogen is titrated no break is discernible. It is necessary, therefore, to choose some definite pH value as the neutralization point. Considering that the chief bases in the titrated residue are calcium, magnesium, and barium and that all of these have comparatively low solution pressures, it seemed best to choose the value 7.00, which is the one used by Bradfield (10)

when $\text{Ba}(\text{OH})_2$ is used. Possibly a value of 7.5 might have been justified. A few typical titration curves are shown in figure 1. Similar curves were made for all samples.

When this direct titration method was used it was found that all soils having pH values above 7.00 contained no exchange hydrogen, whereas, as previously mentioned, ammonium acetate gave exchange H in soils which were definitely alkaline. Some idea of the comparative value of the two methods may be gained by plotting the pH value of the soils with the degree of saturation. The degree of saturation ($100 - \text{H}/\text{T}$) was calculated for each method. This comparison is shown in figures 2 and 3. It is clear that for the soil samples in question a pH value of 7.00 represents 100 per cent saturation when the exchange hydrogen is measured by direct potentiometric titration and 75 to 80 per cent saturation when the exchange H is determined by titrating the ammonium acetate filtrate potentiometrically. Accordingly the direct titration method was adopted, and all calculations in the tables are based on it.

The hydrogen-ion concentration was determined with the quinhydrone electrode on the 1:2 soil—water suspension after the soil and water had been allowed 72 hours to come to equilibrium.

DETERMINATION OF BASES IN THE EXTRACT

The ammonium acetate extract was evaporated on the steam bath with a few drops of nitric acid. The residue was digested once or twice with 5 ml. of aqua regia, for several hours in a covered beaker, the amount and time depending on the quantity of organic matter. Following this it was dehydrated twice with hydrochloric acid, and the chlorides were filtered from the silica. Alumina and iron were removed as hydroxides but were not determined.

Calcium was precipitated in the warm solution containing ammonium chloride with an excess of saturated ammonium oxalate and estimated by titration with potassium permanganate.

The filtrate from the calcium determination was evaporated to dryness in a pyrex beaker, dried in the oven, and gently ignited in the beaker until all ammonium salts were volatilized. The residue was taken up with hydrochloric acid (1 + 4), digested a short time with 20–30 ml. of water, and filtered. The filtrate was made up to a definite volume. One-fourth was taken for the determination of potassium, one-fourth for sodium, and one-half for magnesium.

Magnesium was precipitated as the phosphate and ignited.

Potassium was precipitated as the cobalt nitrite and determined volumetrically by titration with permanganate (34).

Sodium was precipitated as uranyl-zinc-sodium-acetate, dried, and weighed (6, 11).

Exchange ammonium was removed by leaching with 0.1 N HCl. The acid extract was made slightly alkaline with sodium hydroxide and ammonia distilled into standard acid.

When the work was started it was thought that only the limed plots con-

tained any carbonates. When this was investigated it was found that all plots, even the most acid ones, contained carbonate and that ammonium acetate removed a part of the calcium and magnesium in that form. Therefore, carbonates were determined on all samples, before and after leaching with ammonium acetate, and the difference was subtracted from the total calcium in the acetate extract. The latter figure was taken as the true exchangeable calcium, although it is doubtless true that a small part of the carbonate removed was present as magnesium carbonate.

DISCUSSION OF RESULTS

The analytical data are given in a single table in the appendix, together with the treatments and year of sampling. In order to bring out the outstanding

TABLE 1
Soil variation as shown by differences in check plots—Tier 1
(Exchangeable bases in m.e. per 100 gm. soil)

	PLOT 1	PLOT 8	PLOT 14	PLOT 24	PLOT 36	AVERAGE
Year sampled.....	1931	1931	1931	1931	1927	
Total Ca extracted.....	3.98	5.00	4.60	3.27	4.84	4.34
Exchange Ca.....	3.98	4.50	3.85	1.82	3.84	4.00
Mg.....	0.99	1.49	0.57	0.49	0.86	0.88
K.....	0.31	0.25	0.32	0.29	0.29	0.29
Na.....	0.12	0.11	0.09	0.05	0.12	0.10
NH ₄	0.04	0.04	0.03	0.07	0.12	0.06
H.....	1.65	1.00	1.90	4.00	2.60	2.23
Total exchange capacity.....	7.09	7.39	6.76	6.72	7.83	7.15
Saturation, per cent.....	76.7	86.5	71.9	40.5	66.8	68.5
pH.....	6.6	6.8	6.6	6.0	6.2	
Carbonates.....	1.25	2.20	2.05	2.00	1.85	

effects, plots will be grouped side by side, those lying close to one another and in every way comparable being chosen for comparisons.

Soil variation as shown by differences in check plots. Plots 1, 8, 14, 24, and 36 receive no fertilizer, manure, or lime. They may be compared to bring out the soil variation from one end of the field to the other (table 1). The soil is not homogenous because of variations in thickness and density of the strata of limestone, which are tilted. An exposure occurs on plot 8 and accounts for the large quantity of calcium and magnesium on this plot. Plots 3, 5, 6 and especially plot 4, also have areas which are very close to the decomposing limestone. In general the results of these plots in tier 1 will not be used in comparisons but are reported as a matter of record. The acidity increases in plots 14 and 24 but decreases again in plot 36, which adjoins a farm road formerly surfaced with crushed limestone, the dust of which has blown on the plot.

The magnesium content parallels the calcium content and is a fair indication of the nearness to bed rock. The rock contains varying amounts of magnesium carbonate.

The potassium, sodium, and ammonium contents of the five check plots show no consistent variation from one end of the tier to the other.

The exchangeable hydrogen, pH, and degree of saturation are governed by the calcium and magnesium.

These check plots are well supplied with calcium and have an average pH value of about 6.50. Their yields have been poor due to lack of available phosphorus and possibly potassium rather than of available calcium and magnesium.

TABLE 2

Soil variation as shown by differences in grass strips bordering check plots—Tier 1
(Exchangeable bases in m.e. per 100 gm. soil)

Plot bordered Year sampled.....	1 1931	8 1931	14 1931	24 1931	AVERAGE
Total Ca extracted.....	5.93	4.99	5.34	5.26	5.37
Exchange Ca.....	5.43	4.79	4.14	4.96	4.83
Mg.....	1.23	1.40	0.81	0.54	0.99
K.....	0.35	0.44	0.30	0.33	0.35
Na.....	0.11	0.13	0.09	0.10	0.11
NH ₄	0.08	0.14	0.13	0.17	0.13
H.....	0.55	2.38	2.45	4.20	2.40
Total exchange capacity.....	7.75	9.28	7.92	10.30	8.81
Saturation, per cent.....	92.9	74.4	69.1	59.3	73.8
pH.....	6.8	6.4	6.5	6.5	
Carbonates.....	2.6	2.3	2.3	2.3	2.37

Certain grass strips adjacent to plots 1, 8, 14, and 24 were sampled by taking six borings on each side of the plot. The analyses of these samples are given in table 2. The grass strips show less variation than the adjacent cultivated plots, probably because erosion has been more severe on the plot than on the grass strip. The limestone outcrop which causes the Ca and Mg to be high in plot 8 does not appear in the grass strips adjacent to plot 8. The exchange magnesium varies from 0.54 to 1.40 m.e. and is again a good indication of nearness to bed rock.

Effect of cropping, or comparison between untreated plots with adjacent grass strips. This comparison should show the effect of cropping without fertilizer when a rotation of corn, oats, wheat, and clover is used. It brings out the effect of crop residues and of the increase in erosion and leaching, which occurs when land is left bare for certain months in the year. The comparison is not entirely fair since the bluegrass residues are not completely removed from the grass strips, thus allowing the nutrient bases to accumulate.

If we compare each plot with the adjacent grass strip we find (table 3), with one or two minor exceptions, that cropping has resulted in decreased calcium and magnesium contents, very little change in potassium and sodium, but a marked decrease in exchange ammonium. The latter ion stands out, being much higher on the grass strips than in any of the cultivated plots. The total exchange capacity is lowered by cultivation which has encouraged losses of organic matter by decomposition and erosion. In these comparisons we encounter an exception to the general rule, namely, a significant decrease in calcium and magnesium without an increase in hydrogen, which is probably due to a higher organic content on the grass strips.

TABLE 3

Comparison between untreated plots and grass strips between these plots—Tier 1
(Exchangeable bases in m.e. per 100 gm. soil)

	PLOT 1		PLOT 8		PLOT 14		PLOT 24	
	Strips	Plot	Strips	Plot	Strips	Plot	Strips	Plot
Total Ca extract.....	5.93	3.98	4.99	5.00	5.34	4.48	5.26	3.27
Exchange Ca.....	5.43	3.98	4.79	4.50	4.14	3.85	4.96	1.82
Mg.....	1.23	0.99	1.40	1.49	0.81	0.57	0.54	0.49
K.....	0.35	0.31	0.44	0.25	0.30	0.32	0.33	0.29
Na.....	0.11	0.12	0.13	0.11	0.09	0.09	0.10	0.05
NH ₄	0.08	0.04	0.14	0.04	0.13	0.03	0.17	0.07
H.....	0.55	1.65	2.38	1.00	2.45	1.90	4.20	4.00
Total exchange capacity.....	7.75	7.09	9.28	7.39	7.92	6.76	10.30	6.72
Saturation, per cent.....	92.9	76.7	74.4	86.5	69.1	71.9	59.3	40.5
pH.....	6.8	6.6	6.4	6.8	6.5	6.6	6.5	6.0
Carbonates.....	2.6	1.25	2.3	2.2	2.3	2.05	2.3	2.0

Effects of manure. Barnyard manure at the rate of 6, 8, and 10 tons per acre is applied to the corn and oats on plots 16, 18, and 20. The base exchange data from these plots may be compared with those from check plots 14 and 24 (table 4). There seems to be a progressive change in the character of the soil from plot 14 to 24, the latter being definitely more acid. There is a slight indication that the use of manure has decreased the total calcium extracted in ammonium acetate but increased the exchange calcium. The net effect on calcium content of this soil is negligible. The exchange potassium is not increased in spite of the fact that considerable is added in the manure. The total exchange capacity and exchange hydrogen are definitely increased by the use of barnyard manure.

Manuring has tended to build up the magnesium reserve but not at all in proportion to the amounts used.

In conclusion it may be said that the use of manure has chiefly affected the exchange complex by increasing significantly the exchange H, Mg, and total exchange capacity.

Effect of continued use of lime compounds. Only three plots in tiers 1 and 3 have been limed. Plot 22 receives 6 tons of manure and 2 tons of burnt lime on the corn only; plot 23 is limed with 2 tons of burnt lime on corn only; and plot 34 receives 2 tons of ground limestone applied at the time of planting corn and wheat.

Plots 23 and 34 have yielded poorly for several years because of the lack of available phosphorus and possibly nitrogen. The plots have been limed greatly in excess of their needs, but it has never seemed desirable to change the treatments.

When soils are heavily limed repeatedly, as these plots are, they eventually come into equilibrium with calcium carbonate. We have a condition similar to a flask containing solid calcium carbonate in the bottom with a solution of

TABLE 4

Effects of manure—Tier 1

(Exchangeable bases in m.e. per 100 gm. soil)

	PLOT 14	PLOT 16	PLOT 18	PLOT 20	PLOT 24
Treatment.....	None	M6	M8	M10	None
Year sampled.....	1931	1927	1931	1931	1931
Total Ca extracted.....	4.60	4.21	2.59	3.22	3.27
Exchange Ca.....	3.85	4.21	2.19	2.62	1.82
Mg.....	0.57	0.89	0.96	0.66	0.49
K.....	0.32	0.27	0.33	0.38	0.29
Na.....	0.09	0.07	0.11	0.08	0.05
NH ₄	0.03	0.15	0.08	0.08	0.07
H.....	1.90	6.00	5.50	4.70	4.00
Total exchange capacity.....	6.76	11.59	9.17	8.52	6.72
Saturation, per cent.....	71.9	48.2	40.0	44.9	40.0
pH.....	6.6	5.8	5.9	6.0	6.0
Carbonates.....	2.05	1.25	2.5	2.5	2.0

calcium bicarbonate charged with carbonic acid and, above this, air containing a large quantity of carbon dioxide. When this comes into equilibrium it will have a pH value somewhere between 8.2 and 8.4 depending on the temperature and partial pressure of CO₂ in the gas phase. The soil on both the burnt lime and limestone plots has been repeatedly sampled by Professors Holben and Jeffries and by the writer and has been found to fluctuate very little from the pH value 8.25 ± 0.05. However, the writer wished to determine whether or not values higher than these might be encountered immediately after ground burnt lime, CaO, was applied to a soil already containing an excess of calcium carbonate and therefore having a value close to 8.25.

The pH value of saturated lime water at 20°C. was found to be 12.38; therefore, if carbonation is not instantaneous we might expect values considerably above 8.25 for some time after liming. Plots 22, 23, and 34 were limed in the

spring of 1932. The soil was well supplied with moisture at the time, and rains were frequent but not excessive. The pH values were determined on the plots on a few occasions after liming (table 5). It is apparent that under these conditions carbonation is not immediate (28), because the pH value on the burnt lime plot is higher than the equilibrium value of calcium carbonate-

TABLE 5

Effect of liming with burnt lime and with limestone on the pH value of an alkaline soil—Tier 1*

		PLOT 22 CaO MANURE	PLOT 23 CaO	PLOT 34 CaCO ₃
		pH	pH	pH
May 11.....	Moist	N.D.	9.9	8.66
June 15.....	Moist	8.48	8.72	8.48
June 15.....	Dried	8.32	8.32	8.19

* Lime applied May 6 and 7.

TABLE 6.

Effect of lime compounds on the exchangeable bases—Tier 1

(m.e. per 100 gm. soil)

	PLOT 23*	PLOT 23	PLOT 24	PLOT 34*	PLOT 34	PLOT 36
Treatment.....	CaO	CaO	None	CaCO ₃	CaCO ₃	None
Year sampled.....	1932	1927	1931	1932	1931	1927
Total Ca extracted.....	56.2	17.80	3.27	68.0	17.10	4.84
Exchange Ca.....	11.10	8.0	1.82	15.85	11.60	3.84
Mg.....	0.91	0.46	0.49	0.95	0.49	0.86
K.....	0.14	0.38	0.29	0.30	0.38	0.29
Na.....	0.16	0.10	0.05	0.17	0.07	0.12
NH ₄	0.07	0.07	0.09	0.07	0.05	0.12
H.....	0.00	0.00	4.00	0.00	0.00	2.60
Total exchange capacity.....	12.38	9.03	6.72	17.32	12.59	7.83
Saturation, per cent.....	Excess	Excess	40.5	Excess	Excess	66.8
pH.....	8.3	8.3	6.0	8.2	8.4	6.2
Carbonates.....	47.3	29.45	2.0	69.5	43.6	1.85

* Lime as CaO and CaCO₃ was applied in plots 23 and 34 respectively on May 6 and 7, 1932 before sampling.

carbonic acid-carbon dioxide. Injury from over-liming of a soil already neutral or alkaline seems quite possible, provided burnt lime or hydrate is used. Over-liming with carbonate seems less probable.

In table 6 the burnt lime plot 23 is compared with the adjacent check plot 24 and the carbonate of lime plot 34 is compared with the nearest check plot 36. So far as exchange bases are concerned the chief effects of continuous heavy liming have been to build up a large reserve of calcium in the exchange and

carbonate condition and, of course, to eliminate exchange hydrogen. The total exchange capacity as determined by addition is higher on these two plots than on any others in the tier. This might be expected since colloids increase their cation adsorption in the presence of hydroxyl ions (9, 13). However, Schollenberger and Dreibelbis (47) obtained the reverse effect by comparing the total exchange values of the limed and unlimed halves of the Ohio plots. So also did the writer obtain the opposite effect when the limed plots 21, 30, 31, and 32 of tier 2 are compared with the corresponding unlimed plots in tier 1 (table 14). In each of these latter cases there is a decrease of from 1 to nearly 3 m.e. in total capacity resulting from liming tier 2 in 1921. In the latter cases, where liming has caused a decrease in total capacity, the pH value is not above 7.00. In the former case, where excessive liming was practiced, the pH

TABLE 7

Effect of the superphosphate-muriate of potash treatment upon the exchangeable bases
(m.e. per 100 gm. soil)

	PLOT 8	PLOT 7	PLOT 14	PLOT 15	PLOT 24	PLOT 25	PLOT 36	PLOT 29
Treatment.....	0	P + K	0	P + K	0	P + K	0	P + K
Year sampled.....	1931	1931	1931	1931	1931	1931	1927	1932
Total Ca extract.....	5.00	4.48	4.60	3.82	3.27	3.00	4.84	2.96
Exchange Ca.....	4.50	4.13	3.85	3.12	1.82	3.00	3.84	2.96
Mg.....	1.49	1.55	0.57	0.49	0.49	0.48	0.86	0.88
K.....	0.25	0.49	0.32	0.46	0.29	0.50	0.29	0.53
Na.....	0.11	0.21	0.09	0.11	0.05	0.05	0.12	0.48
NH ₄	0.04	0.05	0.03	0.07	0.07	0.21	0.12	0.16
H.....	1.00	2.30	1.90	3.75	4.00	6.40	2.60	4.45
Total exchange capacity.....	7.39	8.73	6.76	8.00	6.72	10.64	7.83	9.46
Saturation, per cent.....	86.5	73.6	71.9	53.2	40.5	39.9	66.8	53.0
pH.....	6.8	6.7	6.6	6.35	6.0	5.2	6.2	6.1
Carbonates.....	2.2	2.8	2.05	2.2	2.0	1.35	1.85	1.16

values were about 8.3. Exchange magnesium has been increased by liming, but no significant difference appears with respect to the other cations.

Influence of superphosphate-muriate of potash treatment on exchangeable base content. Plots 7, 15, 25, and 29 receive 300 pounds of 16 per cent superphosphate and 200 pounds of muriate of potash twice in the rotation. The quantity of potash is believed to be excessive. Nevertheless, this combination has given the largest net financial returns of any combination used, with the exception of those receiving barnyard manure. Fortunately for study, each of these plots lies adjacent to, or close to, a check plot. The comparisons are given in table 7. In making such comparisons we must keep in mind that the yields on the nothing plots have been small for several years, while those on the PK plots have been large, hence there will be a greater removal of the nutrient bases on the PK plots. Furthermore superphosphate contains calcium as phosphate and sulfate, and this should tend to maintain the supply of this element.

The total exchange capacity has been increased by the PK treatment in every instance, doubtless as a result of the higher organic content which these plots have attained. At the same time active organic matter has declined on the nothing plots on account of the smaller crop residues.

The total calcium extracted with ammonium acetate is significantly lower in every case as a result of the PK treatment. This is true in spite of the fact that calcium is added in the superphosphate. The exchange calcium is also decreased by this fertilizer combination in all except one case. Nothing definite can be said about the exchange magnesium, but potassium has been nearly doubled, as would be expected. Concomitant with the decrease of calcium we have a positive gain in hydrogen in the colloidal matter. The PK treated plots are less saturated with bases and have slightly lower pH values. It is

TABLE 8

Influence of superphosphate alone upon the exchangeable bases
(m.e. per 100 gm. soil)

	PLOT 1	PLOT 3	PLOT 8
Treatment.....	None	P	None
Year sampled.....	1932	1932	1932
Total Ca extracted.....	4.42	4.49	4.24
Exchange Ca.....	3.57	3.64	3.74
Mg.....	1.68	1.14	1.33
K.....	0.30	0.14	0.23
Na.....	0.11	0.11	0.12
NH ₄	0.04	0.02	0.06
H.....	2.00	2.70	2.10
Total exchange capacity.....	7.70	7.75	7.58
Saturation, per cent.....	74.0	62.7	72.3
pH.....	6.5	6.2	6.5
Carbonates.....	1.4	1.45	1.15

not altogether fair to compare PK plot 29 with the check 36 because the latter receives limestone dust from the highway, but if we compare it with check plot 24, which is closer to it, the conclusions are nearly the same.

No explanation is given for the high exchange sodium content on PK plot 29, and no importance is claimed for it. The duplicate determinations on this plot gave 0.50 and 0.46 m.e. of sodium.

Effect of superphosphate alone. The PK combination was shown to cause a decrease in calcium and an increase in hydrogen, but it was not possible to determine which salt was responsible for the change. Plot 3 of tier I receives superphosphate alone, but the soil is not uniform enough to be considered. However, the first eight plots in tier 3, also unlimed, are very homogenous, hence plot 3 receiving superphosphate alone is compared with check plots 1 and 8 tier 3 (table 8). Analyses of the data indicate that superphosphate has had very little effect upon the reactive calcium but it has produced a

significant increase in exchange hydrogen. This is in agreement with the findings of Schollenberger and Dreibelbis (47) and of Page and Williams (36). Exchange magnesium and potassium are decreased by the use of superphosphate alone, doubtless because of the greater removal in crops, which have been sizeable on this plot. The phosphate has decreased the state of saturation with bases by about 10 per cent and increased the hydrogen-ion concentration. It is concluded that superphosphate does tend to increase acidity even though it increases the active calcium in the soil. The effect is a small one for 50 years of continuous use.

Comparison between raw bone and acidulated phosphates. From theoretical considerations it would seem that raw bone might decrease acidity if the PO_4 ,

TABLE 9

Comparison between ground bone and superphosphate upon the content of exchangeable bases (m.e. per 100 gm. soil)

	PLOT 6*	PLOT 12	PLOT 17	PLOT 19	PLOT 35
Treatment.....	NK	NPK	NPK	NPK	NPK
P carrier.....	None	Bone	Superphosphate	Superphosphate	Bone
Year sampled.....	1931	1931	1931	1931	1932
Total Ca extracted.....	3.47	4.31	1.66	1.74	5.11
Exchange Ca.....	3.32	3.21	0.81	1.34	5.11
Mg.....	1.28	1.37	0.47	0.30	1.57
K.....	0.66	0.43	0.44	0.40	0.56
Na.....	0.18	0.14	0.12	0.08	0.21
NH_4	0.05	0.05	0.08	0.08	0.10
H.....	2.55	2.90	6.20	6.40	1.95
Total exchange capacity.....	8.04	8.10	8.12	8.60	9.50
Saturation, per cent.....	68.3	64.2	23.7	25.6	79.5
pH.....	6.6	6.6	5.6	5.5	5.6
Carbonates.....	1.60	6.40	2.90	2.10	1.67

* Not a good comparison plot. Probably influenced by nearness to limestone in places.

HPO_4 , or H_2PO_4 ion is assimilated in greater equivalent quantity than calcium. On the other hand superphosphate contains an acid salt $\text{Ca H}_4(\text{PO}_4)_2$ with three equivalents of PO_4 for each equivalent of calcium. It should increase acidity and was shown to in plot 3 of tier 3.

To compare these two carriers of phosphorus we may use plots 12 and 35 vs. 17 and 19 in tier 1. Plots 12 and 35 each receive 30 pounds of nitrogen in blood, 48 pounds of P_2O_5 in ground bone, and 100 pounds of K_2O in muriate of potash. Plots 17 and 19 are treated like 12 and 35 except that they receive their phosphorus in superphosphate and have slightly different amounts of blood—17 receives 24 pounds, and 19 receives 48 pounds of nitrogen (table 9).

Ground bone appears to have left a residue of calcium in the soil, hence even though slightly more of the acid forming blood is applied to bone plots 12

and 35 than to the superphosphate plot, still there is definitely more calcium in the bone treated plots. The exchange hydrogen, saturation values, and pH values all prove that superphosphate increases soil acidity as compared with ground bone. The exchange magnesium is likewise lower in the superphosphate plots.

Further evidence is gained when plot 6, which receives blood and muriate, is compared with plot 17, which is fertilized with superphosphate in addition, or with plot 12 or 35, both of which receive bone in addition. These comparisons prove that bone builds up a reserve of calcium with little or no effect upon the exchange hydrogen and pH value. It is also apparent that superphosphate does increase soil acidity. The nitrogen-potash plot 6 appears to contain a

TABLE 10

Effect of dried blood upon the exchangeable bases (m.e. per 100 gm. soil)

Tier and plot.....	3/1 O	3/2 N	3/8 O	1/15 PK	1/17 NPK	1/19 NPK	1/21 NPK	1/25 PK
Treatment.....	0	24	0	0	24	48	72	0
N per acre, lbs.....								
Total Ca extracted.....	4.42	3.40	4.24	3.82	1.66	1.74	1.72	3.00
Exchange Ca.....	3.57	2.68	3.74	3.12	0.81	1.34	0.92	3.00
Mg.....	1.68	1.14	1.33	0.49	0.47	0.30	0.29	0.48
K.....	0.30	0.25	0.23	0.46	0.44	0.40	0.48	0.50
Na.....	0.11	0.11	0.12	0.11	0.12	0.08	0.14	0.05
NH_4	0.04	0.04	0.06	0.07	0.08	0.08	0.11	0.21
H.....	2.00	3.44	2.10	3.75	6.20	6.40	7.40	6.40
Total exchange capacity.....	7.70	7.66	7.58	8.00	8.12	8.60	9.34	10.64
Saturation, per cent.....	74.0	55.1	72.3	53.2	23.7	25.6	20.8	39.9
pH.....	6.5	5.8	6.5	6.35	5.6	5.5	5.5	5.2
Carbonates.....	1.40	1.50	1.15	2.20	2.90	1.34	2.1	1.35

reserve of magnesium and potassium which is due to the low removals in crops from this plot.

Schollenberger's data (47) reveal no appreciable difference between bone and superphosphate in the quantity of adsorbed ions.

Effect of dried blood used alone. Dried blood contains 16 per cent nitrogen, most of which is easily nitrified. Its total ash content is low, consequently, on decay, carbonic and nitric acids are formed, and acids even when present in low concentration possess high base exchange powers due to the high energy of absorption of the hydrogen ion. We therefore expect a considerable loss of bases as a result of the use of dried blood without lime. This is shown to be the case in the comparisons which follow:

Table 10 is a comparison between the untreated check plots 1 and 8 and the blood treated plot 3, in tier 3. The yields on plot 3 (blood) have been poor, in fact lower than the average of the five check plots. Consequently, any decrease in bases as compared with the checks is due to leaching rather than to

crop removal. Dried blood has caused a decided decrease in the quantity of calcium and magnesium and a corresponding increase in replaceable hydrogen. The remaining exchangeable cations are unaffected.

In tier 1 it is possible to compare three rates of dried blood with the nearest PK plots; the only variant being the presence and amount of blood. Plots 17, 19, and 21 receive 24, 48, 72 pounds of nitrogen respectively in blood, twice in the rotation. The use of blood, as might be expected, has caused a decided decrease in total extracted calcium and exchangeable calcium to about one-half or one-third of that in the nearest PK plots. However, there is no evidence that the larger amounts of blood have been more effective in reducing the active calcium than have smaller amounts, or to put it another way, the smaller amounts of blood have reduced the calcium to such a low figure that larger amounts show no added effect. It is logical to assume that during the 50 years more nitrogen has found its way into the drainage water as HNO_3 in plot 21 than in plot 17. It is obviously impossible to calculate in advance how much lime must accompany a given quantity of blood to keep a soil in its original state of saturation.

The exchange magnesium is also decreased by the use of blood. No significant differences are to be found in the quantity of adsorbed potassium. Equal, large amounts of this element have been added to all plots in this comparison; and in spite of the large amount removed in crops there are now 0.40 to 0.50 m.e. present.

The PK plots 15 and 25 are now 40 to 50 per cent saturated with bases, whereas those receiving blood in addition are only 20 to 25 per cent saturated.

Organic nitrogen has produced upon the exchange picture of this soil a profound effect that is now showing itself in reduced yields on these plots even though heavily fertilized. Liming on tiers 2 and 4 has completely restored this soil in character of complex and in yields.

Effect of the use of nitrate of soda. According to theoretical reasoning and the observations handed down to us from the majority of field experiments (19) nitrate of soda either should have no effect or should reduce acidity slightly. Both ions of this salt leach readily. The sodium will seek the liquid phase and leach out with any strong acid radicals, which may be added to, or formed in, the soil.

Plots 26, 27, and 28, which receive nitrate of soda equivalent to 24, 48, and 72 pounds of nitrogen, and the adjacent PK plots 25 and 29 are used in this comparison. The only variable is the presence and amount of nitrate of soda. This comparison is given in table 1. The use of nitrate of soda has had no appreciable effect upon the quantity of any ion except hydrogen, which has been slightly reduced. Sodium has not been retained; therefore, the total exchange capacity of the soda-treated soils is lowered by 2 or 3 m.e. It is logical to assume that sodium has peptized some of the colloidal matter and caused it to be translocated to lower horizons or removed in the drainage water.

These effects of nitrate of soda agree exactly with those reported by Schollenberger (47).

No explanation is offered for the high sodium content found in the PK plot 29. Pierre (41, 42) has reported a tendency for nitrate of soda to increase alkalinity as shown by pH values and by degree of saturation, but his work was conducted in greenhouse pots, in which no leaching took place. Under such conditions a sodium residue is permitted to accumulate.

Influence of sulfate of ammonia. This fertilizer salt is well known for its effects upon soil reaction, although it should be pointed out that for the first 8 years of this experiment (39) the sulfate plots outyielded the nitrate or blood plots and it was not until 20 years had elapsed that the yield dropped

TABLE 11
Effects of nitrate of soda upon the exchangeable bases
(m.e. per 100 gm. soil)

	PLOT 25	PLOT 26	PLOT 27	PLOT 28	PLOT 29
Treatment.....	PK	NPK	NPK	NPK	PK
N per acre, lbs.....	0	24	48	72	0
Year sampled.....	1927	1931	1931	1931	1932
Total Ca extracted.....	3.00	3.18	3.43	2.91	2.96
Exchange Ca.....	3.00	2.98	3.33	2.76	2.96
Mg.....	0.48	0.54	0.52	0.35	0.88
K.....	0.50	0.41	0.42	0.48	0.53
Na.....	0.05	0.14	0.10	0.11	0.48
NH ₄	0.21	0.10	0.09	0.08	0.16
H.....	6.40	4.20	4.00	4.20	4.45
Total exchange capacity.....	10.64	8.37	8.46	7.98	9.46
Saturation, per cent.....	39.9	49.8	52.7	47.4	53.0
pH.....	5.2	6.0	6.1	6.0	6.0
Carbonates.....	2.45	1.60	1.2	1.05	1.3

materially on account of acidity. Furthermore, one treatment with lime on tiers 2 and 4 has completely restored the fertility on these very acid plots.

The theoretical reasoning has been put forth by Pierre (41, 42), by Allison (2), and by Kappan, (24, 25) that if all the ammonia in sulfate of ammonia is transformed into nitric acid, each equivalent of sulfate of ammonia produces two equivalents of acid and on this basis the lime needs may be calculated. Under field conditions when sulfate of ammonia is applied to different crops and with varying climatic conditions, we are confronted with such questions as: What proportion of the total nitrogen is assimilated in the ammonia form and what part in the nitrate form (50), and is this the same for all plants? What proportion of the nitrogen which leaches out is in the form of nitrate salts and what part is in the form of nitric acid? Can plants assimilate nitric acid (2), that is, can they adsorb anions in excess of cations? All these ques-

tions made it utterly impossible to calculate the amount of lime needed under field conditions for each 100 pounds of sulfate of ammonia.

Plots 29, 30, 31, and 32 in tier 1 were chosen for this comparison. Plot 29 is the PK plot, the remaining plots receive, in addition to PK, varying amounts of sulfate of ammonia. Plot 29 was sampled in 1932; plots 30, 31, and 32 were sampled in 1931; and plot 32 was also sampled in 1927. These comparisons are set forth in table 12.

Sulfate of ammonia has produced the most marked effects of any fertilizer used in this experiment. The total calcium extractable and the exchange calcium have been reduced to one-third by the use of 24 pounds of nitrogen in sulfate of ammonia twice in the rotation, and to about one-fourth and one-

TABLE 12
Effects of sulfate of ammonia upon the quantity of exchangeable bases
(m.e. per 100 gm. soil)

	PLOT 29	PLOT 30	PLOT 31	PLOT 32	PLOT 32
Treatment.....	PK	NPK	NPK	NPK	NPK
N per acre, lbs.....	0	24	48	72	72
Year sampled.....	1932	1931	1931	1931	1927
Total Ca extracted.....	2.96	1.31	0.73	0.75	0.45
Exchange Ca.....	2.96	1.31	0.38	0.65	0.45
Mg.....	0.88	0.31	0.33	0.31	0.59
K.....	0.53	0.33	0.38	0.38	0.29
Na.....	0.48	0.15	0.11	0.07	0.18
NH ₄	0.16	0.11	0.10	0.07	0.14
H.....	4.45	6.60	8.10	8.80	8.70
Total exchange capacity.....	9.46	8.81	9.40	10.28	10.33
Saturation, per cent.....	53.0	25.0	13.8	14.5	15.5
pH.....	6.1	5.3	4.96	4.70	4.55
Carbonates.....	1.3	0.9	1.3	0.7	0.75

sixth, respectively, by the 48-pound and 72-pound applications. From 75 to 85 per cent of all the exchange ions are hydrogen ions, but calcium is not the only base affected. Magnesium and even potassium have been significantly diminished, when compared with the nearest PK plot. This is true in spite of the fact that equal, large amounts of potash have been used and that the crop removals on the most acid plots have not been as great as on the PK plots. The average exchange potassium content of the three corresponding blood plots is 0.44, and of the three nitrate plots 0.44, whereas the three sulfate of ammonia plots average only 0.36. This difference is not large but is quite consistent. It appears impossible to calculate the lime needs from any factor or formula, since the 48-pound application has depleted the calcium as much as the 72-pound treatment. It seems logical that the more calcium that is present in the soil the more rapidly it will be removed, and that, when the active

calcium content is reduced to a very low figure, the nitric and sulfuric acid may leach through as acids or even as iron and alumina salts. This was well brought out in a previous paper by the writer (32), in which the base exchange content of samples drawn in 1915 was compared with that of those drawn in 1927. Some data are reproduced in table 13. During the 12-year period from 1915 to 1927 the loss of calcium and magnesium has been no greater on the sulfate of ammonia plot 32 than upon the phosphorus-potash plot 25. This is because early in the history of the experiment the sulfate of ammonia had replaced the readily replaceable calcium with hydrogen ions.

It is interesting to note that some carbonates are present even in the most acid plot, No. 32. This plot has had a pH value of 4.5 to 4.7 for several years.

TABLE 13
Comparison of different nitrogen carriers with the PK plot in 1915 and 1927
(Exchangeable bases in m.e. per 100 gm. soil)

	PK 25	NPK NaNO ₃ 28	NPK Blood 21	NPK (NH ₄) ₂ SO ₄ 32
Calcium 1915.....	4.07	3.73	3.34	1.51
Calcium 1927.....	3.00	3.12	2.30	0.45
12-year change.....	-1.07	-0.61	-1.04	-1.06
Magnesium 1915.....	0.75	0.81	0.74	0.87
Magnesium 1927.....	0.48	0.55	0.55	0.59
12-year change.....	-0.27	-0.26	-0.19	-0.28
Hydrogen 1915*.....	5.25	4.22	5.87	6.02
Hydrogen 1927.....	6.05	5.50	7.22	8.65
12-year change.....	+0.80	+1.28	+1.35	+2.63

* Exchange hydrogen determined by ammonium acetate extraction.

The carbonate content of the sulfate of ammonia plots is lower than that of any other plot in this field experiment.

There is no evidence that sulfate of ammonia causes the NH₄ ion to accumulate in the colloidal complex.

It is quite probable that these plots will not attain pH values much lower than 4.5 even though the use of sulfate of ammonia be continued. Under the conditions obtaining here, the nitric and sulfuric acids added and formed from each application will leach through as acids or as iron and aluminum salts, and the pH value will revert to that of humic and silicic acids. For a few months after fertilization the pH value may possibly run lower than 4.5. This has not been investigated.

The base exchange picture on these sulfate-treated plots is decidedly different from that of those receiving P and K and consists in the substitution of H for not only Ca but for Mg and K also.

Effect of muriate of potash. It was previously shown that the PK treatment had acid-producing tendencies but it remained to be determined which salt in this combination was responsible. Then it was shown that superphosphate alone tended to increase the replaceable hydrogen but not to reduce the replaceable calcium materially. What is the effect of the potash salt?

Plot 4 in tier 1 might have been chosen to make this comparison but, since it is probably the least uniform of all plots sampled in this work, plot 4, KCl alone, in tier 3 was compared with check plots 1 and 8 in the same tier (table 14). The addition of K as KCl has caused a reduction in total calcium extracted and in exchangeable calcium, no effect upon magnesium, but a decided increase in potassium. In this case K rather than H seems to have replaced the Ca, for there is no increase in replaceable H. Yields have been low on this plot because

TABLE 14
Effects of muriate of potash on the content of exchangeable bases
(m.e. per 100 gm. soil)

Tier and plot.....	3/1 O 1932	3/4 K 1932	3/8 O 1932	1/2 N 1927	1/6 NK 1931
Treatment.....					
Year sampled.....					
Total Ca extracted.....	4.42	3.64	4.24	5.69	3.47
Exchange Ca.....	3.57	2.99	3.74	5.69	3.32
Mg.....	1.68	1.39	1.33	1.83	1.28
K.....	0.30	0.68	0.23	0.23	0.66
Na.....	0.11	0.14	0.12	0.20	0.18
NH ₄	0.04	0.06	0.06	0.05	0.05
H.....	2.00	2.10	2.10	0.00	2.55
Total exchange capacity.....	7.70	7.36	7.58	8.00	8.04
Saturation, per cent.....	74.0	71.5	72.3	Excess	68.3
pH.....	6.5	6.5	6.5	7.2	6.6
Carbonates.....	1.40	1.45	1.15	1.85	1.6

of lack of available phosphorus, hence the large reserve of potassium. Any plot in this experiment which receives no phosphate, yields poorly. The decrease in Ca either has been insufficient to make any difference in pH value or it is counterbalanced by the more highly dissociating potassium.

In tier 1, plot 2 may be compared with plot 6. Both receive dried blood equal to 24 pounds of nitrogen, the variable being muriate of potash. Although these results cannot be regarded as very conclusive, because of the soil irregularity previously mentioned, they do tend to confirm the conclusion drawn from tier 3, plot 1, 4, 8, namely, that the addition of KCl causes calcium depletion and the building up of a reserve of exchange K.

The same conclusions are strengthened by comparing plot 5, blood and superphosphate, with plot 12, blood, bone, and muriate, though in this case the source of phosphorus is different in the two plots compared.

Effect of recent liming on certain very acid plots. In 1921, tier 2 was limed

according to the lime requirement as determined by Prof. J. W. White and his associates. The yields on the acid plots were quickly restored. There was some reserve of phosphorus, due to a long period of low yields, but no special reserve of magnesium and potassium. It is interesting to find the chief effect brought about by liming these very acid plots. A few of the most acid plots—the sulfate of ammonia plots and the plot receiving the highest blood treatment—have been compared with the corresponding unlimed plots in tier 1 (table 15).

In each of these acid plots, liming restored the exchangeable calcium from almost nothing in tier 1 to from 4 to 6 m.e. in tier 2. It would appear that for this soil from 4.0 to 4.5 m.e. of calcium in the exchange form are necessary to produce neutrality.

TABLE 15
Effect of recent liming on certain very acid plots—Tiers 1 and 2

	PLOT 21		PLOT 30		PLOT 31		PLOT 32	
Treatment.....	NPK		NPK		NPK		NPK	
N per acre, lbs.....	Blood, 72 lbs. N		Sulfate, 24		Sulfate, 48		Sulfate, 72	
Tier and liming.....	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
Year sampled.....	1931	1932	1931	1932	1931	1932	1931	1932
Total Ca extract.....	1.72	5.82	1.31	7.13	0.73	6.70	0.75	6.60
Exchange Ca.....	0.92	5.82	1.31	3.90	0.38	5.23	0.65	4.65
Mg.....	0.29	0.89	0.31	1.53	0.33	1.51	0.31	1.33
K.....	0.48	0.45	0.33	0.32	0.38	0.37	0.38	0.53
Na.....	0.14	0.13	0.15	0.14	0.11	0.12	0.07	0.12
NH ₄	0.11	0.06	0.11	0.04	0.10	0.07	0.07	0.15
H.....	7.40	0.89	6.60	0.00	8.10	0.00	8.80	0.00
Total exchange capacity..	9.34	8.24	8.81	5.93	9.40	7.30	10.28	6.78
Saturation, per cent.....	20.8	89.2	25.0	Excess	13.8	Excess	14.5	Excess
pH.....	5.5	6.8	5.3	7.3	4.96	7.15	4.70	7.00
Carbonates.....	2.10	1.1	0.90	7.03	0.95	2.87	0.70	2.80

The magnesium, which had likewise been reduced to around 0.29 to 0.33 m.e. by acid-producing fertilizers, was restored by the liming materials used, which contain small amounts of magnesium.

Potassium, sodium, and ammonia seem not to have been materially influenced by liming.

In only one case, that of plot 30 in tier 2, is there any marked excess of calcium carbonate over the general average of all the plots. In this case we have limed in excess of the true lime requirement.

These treatments have restored the yields. It would have been highly instructive to see what effects fractional neutralization would have had on yields and on exchange complex.

In choosing these plots in tier 1 and 2, it was thought that we might shed some light on the important question of whether or not all the H must be

replaced in the complex for best results with these crops. It was shown that the H was replaced, at least according to the methods used, but whether or not smaller amounts of lime would give equal yields is not demonstrated.

Comparison of nitrogen carriers. The three nitrogen carriers, dried blood, nitrate of soda, and sulfate of ammonia, each in sufficient quantity to carry 72 pounds of nitrogen per acre twice in the rotation are compared with one another and with the nearest PK plots. In this comparison the PK treatments are alike throughout. To show the trend of the soil as well as our data permit, the plots are arranged in table 16 in the order in which they occur in the field.

The comparisons show that nitrate of soda has very little effect upon the exchange Ca, Mg, and H; upon saturation; or upon pH value. Dried blood

TABLE 16
A comparison of nitrogen carriers—Tier 1, 72 pounds N per acre
(Exchangeable bases in m.e. per 100 gm. soil)

	PLOT 15	PLOT 21	PLOT 25	PLOT 28	PLOT 29	PLOT 32
Treatment.....	PK	NPK	PK	NPK	PK	NPK
N carrier.....	O	Blood	O	Nitrate	O	Sulphate
Year sampled.....	1931	1931	1927	1931	1932	1931
Total Ca extract.....	3.82	1.72	3.00	2.91	2.96	0.75
Exchange Ca.....	3.12	0.92	3.00	2.76	2.96	0.65
Mg.....	0.49	0.29	0.48	0.35	0.88	0.31
K.....	0.46	0.48	0.50	0.48	0.53	0.38
Na.....	0.11	0.14	0.05	0.11	0.48	0.07
NH ₄	0.07	0.11	0.21	0.08	0.16	0.07
H.....	3.75	7.40	6.40	4.20	4.45	8.80
Total exchange capacity.....	8.00	9.34	10.64	7.98	9.46	10.28
Saturation, per cent.....	53.2	20.8	39.9	47.4	53.0	14.5
pH.....	6.35	5.5	5.2	6.0	6.1	4.7
Carbonates.....	2.20	2.10	2.45	1.1	1.3	0.70

decidedly increases acidity, and sulfate of ammonia greatly affects not only Ca and Mg but exchange K as well.

Relation between pH value and degree of saturation. The pH value of a soil is a measure of the ratio between the active cations and anions in the soil solution, which in turn are controlled by the adsorbed ions. One might expect, therefore, for any given soil, a fairly definite relationship between the degree of saturation and the pH value. Conrey and Schollenberger (16) obtained a fair relationship between pH value and degree of saturation of the various horizons of the Claremount soil profile. If the data of Walker, Firkins, and Brown (51) are examined with this in view a very good correlation is found.

Since both values were determined in this work it was thought well to plot one against the other to see how close the relationship is for this soil. Figure 3 shows this relationship for degrees of saturation calculated from exchange

hydrogen as determined by titrating the ammonium acetate extract, and figure 2 shows the relationship when exchange hydrogen is determined by direct titration of the soil with Ba(OH)₂.

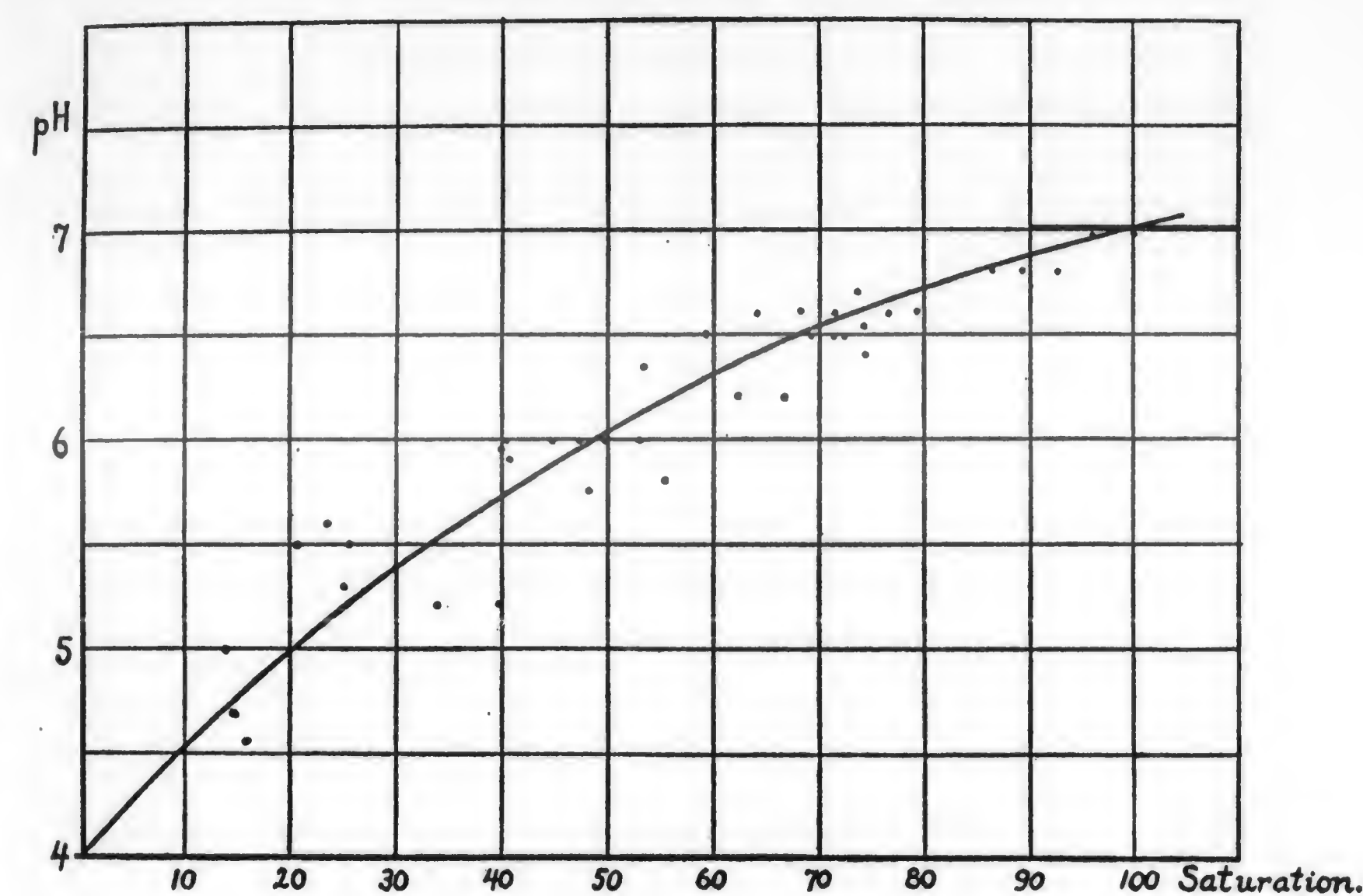


FIG. 2. RELATION BETWEEN pH AND SATURATION
Exchange H by direct titration

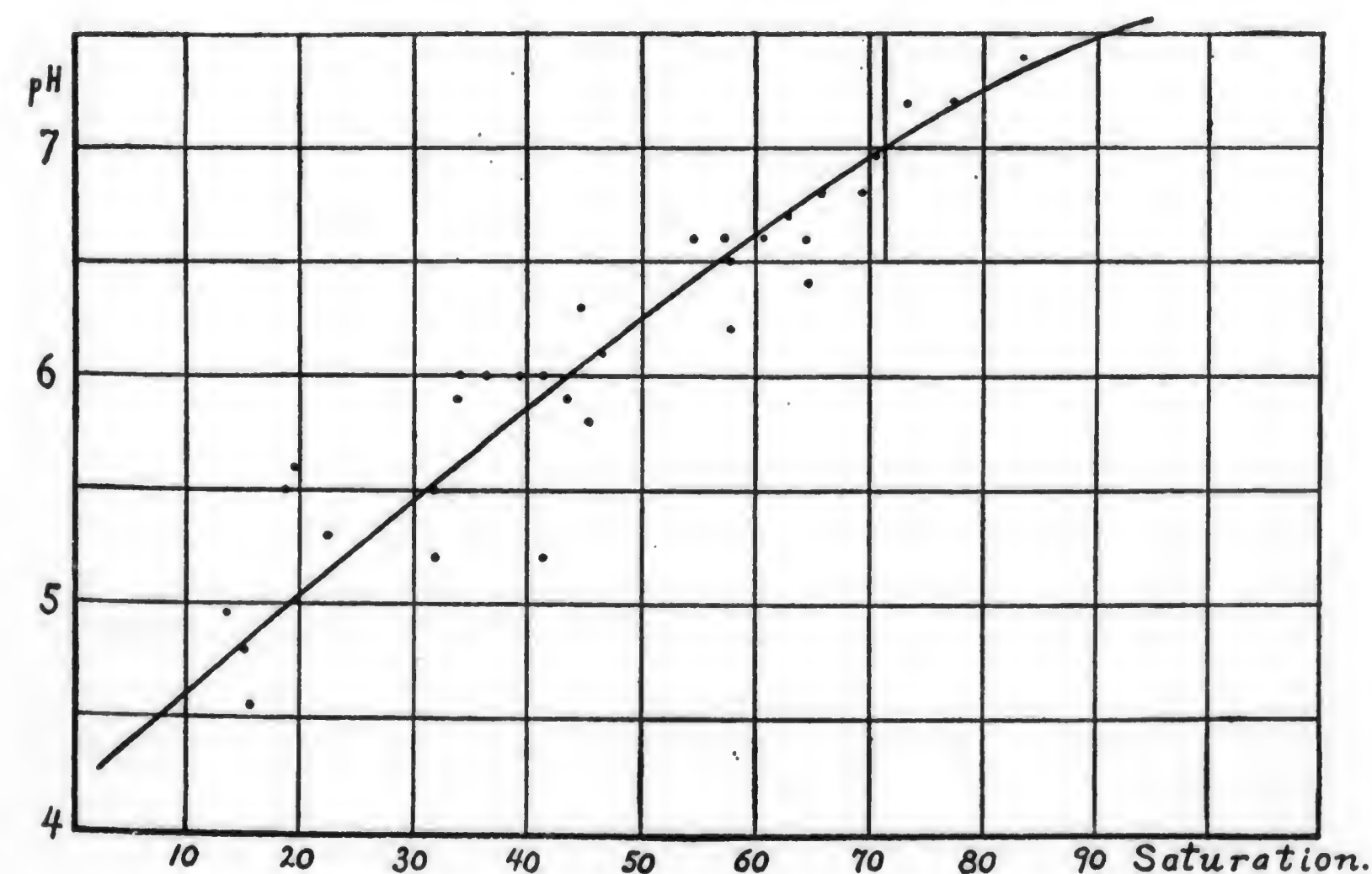


FIG. 3. RELATION BETWEEN pH AND DEGREE OF SATURATION
Exchange H by ammonium acetate

TABLE 17

Summary table showing the exchangeable cations in the Pennsylvania Jordan soil fertility plots after 45-50 years of continuous cropping and fertilizing
(Exchangeable ions in m.e. per 100 gm. soil)

TIER	PLOT	FERTILIZERS ALTERNATE YEARS	TOTAL Ca EX- TRACTED	Ca	Mg	K	Na	NH ₄	H TITRA- TION	H NH ₄ Ac	TOTAL	TOTAL CO ₂	PER CENT SATU- RATION	pH	YEAR SAMPLED
1	1	None, strips	5.93	5.43	1.23	0.35	0.11	0.08	0.55	3.17	7.75	2.60	92.9	6.8	1931
1	1	None	3.98	3.98	0.99	0.31	0.12	0.04	1.65	3.50	7.09	1.25	76.7	6.6	1931
1	2	Nb24	5.69	5.69	1.83	0.23	0.20	0.05	0.00	2.30	8.00	1.85	100+	7.2	1927
1	3	P	6.31	6.21	2.02	0.29	0.10	0.09	0.00	3.15	8.71	1.45	100+	7.1	1927
1	4	K	6.31	6.31	3.13	0.31	0.29	0.06	0.00	2.00	10.10	6.15	100+	7.4	1927
1	5	Nb24, P	5.48	4.98	1.82	0.34	0.09	0.07	0.30	3.10	7.60	2.80	96.1	7.0	1931
1	6	Nb24, K	3.47	3.32	1.28	0.66	0.18	0.05	2.55	4.05	8.04	1.60	68.3	6.6	1931
1	7	P, K	4.48	4.13	1.55	0.49	0.21	0.05	2.30	3.80	8.73	2.80	73.6	6.7	1931
1	8	None, strips	4.99	4.79	1.40	0.44	0.13	0.14	2.38	3.70	9.28	2.30	74.4	6.4	1931
1	8	None	5.00	4.50	1.49	0.25	0.11	0.04	1.00	3.32	7.39	2.20	86.5	6.8	1931
1	12	Nb30, Pb, K	4.31	3.21	1.37	0.43	0.14	0.05	2.90	4.40	8.10	6.40	64.2	6.6	1931
1	14	None, strips	5.34	4.14	0.81	0.30	0.09	0.13	2.45	3.99	7.92	2.30	69.1	6.5	1931
1	14	None	4.60	3.85	0.57	0.32	0.09	0.03	1.90	4.22	6.76	2.05	71.9	6.6	1931
1	15	P, K	3.82	3.12	0.49	0.46	0.11	0.07	3.75	5.27	8.00	2.20	53.2	6.35	1931
1	16	M6	4.21	4.21	0.89	0.27	0.07	0.15	6.00	6.75	11.59	1.25	48.2	5.8	1927
1	17	Nb24, P, K	1.66	0.81	0.47	0.44	0.12	0.08	6.20	7.75	8.12	2.90	23.7	5.6	1931
1	18	M8	2.59	2.19	0.96	0.33	0.11	0.08	5.50	7.15	9.17	2.50	40.0	5.95	1931
1	19	Nb48, P, K	1.74	1.34	0.30	0.40	0.08	0.08	6.40	7.91	8.60	2.10	25.6	5.5	1931

1	20	M-10	3.22	2.62	0.66	0.38	0.08	0.08	4.70	6.63	8.52	2.50	44.9	6.0	1931
1	21	Nb72, P, K	1.72	0.92	0.29	0.48	0.14	0.11	7.40	8.40	9.34	2.10	20.8	5.5	1931
1	22	M6, CaO	52.10	12.80	1.37	0.26	0.22	0.05	0.00		14.70	42.3	100+	8.3	1932
1	23	CaO	17.80	8.00	0.46	0.38	0.10	0.09	0.00		9.03	29.45	100+	8.3	1927
1	23	CaO	56.20	11.10	0.91	0.14	0.16	0.07	0.00		12.38	47.30	100+	8.3	1932
1	24	None, strips	5.26	4.96	0.54	0.33	0.10	0.17	4.20	4.61	10.30	2.30	59.3	6.5	1931
1	24	None	3.27	1.82	0.49	0.29	0.05	0.07	4.00	5.17	6.72	2.00	40.5	6.0	1931
1	25	P, K	3.00	3.00	0.48	0.50	0.05	0.21	6.40	6.05	10.64	2.45	39.9	5.2	1927
1	26	Nn24, P, K	3.18	2.98	0.54	0.41	0.14	0.10	4.20	5.85	8.37	1.60	49.8	6.05	1931
1	27	Nn48, P, K	3.43	3.33	0.52	0.42	0.10	0.09	4.00	5.10	8.46	1.20	52.9	6.1	1931
1	28	Nn72, P, K	3.12	3.07	0.55	0.39	0.08	0.14	6.20	5.50	10.43	1.05	40.6	5.9	1927
1	28	Nn72, P, K	2.91	2.76	0.35	0.48	0.11	0.08	4.20	5.90	7.98	1.10	47.4	6.0	1931
1	29	P, K	2.96	2.96	0.88	0.53	0.48	0.16	4.45	N D	9.46	1.30	53.0	6.1	1932
1	30	Ns24, P, K	1.31	1.31	0.31	0.33	0.15	0.11	6.60	7.71	8.81	0.90	25.0	5.3	1931
1	31	Ns48, P, K	0.73	0.38	0.33	0.38	0.11	0.10	8.10	8.34	9.40	1.30	13.8	4.96	1931
1	32	Ns72, P, K	0.45	0.45	0.59	0.27	0.18	0.14	8.70	8.65	10.33	0.75	15.5	4.5	1927
1	32	Ns72, P, K	0.75	0.65	0.31	0.38	0.07	0.07	8.80	8.40	10.28	0.70	14.5	4.7	1931
1	34	CaCO ₃	17.10	11.60	0.49	0.38	0.07	0.05	0.00		12.59	43.60	100+	8.4	1931
1	34	CaCO ₃	68.00	15.85	0.95	0.30	0.17	0.05	0.00		17.32	69.50	100+	8.2	1932
1	35	Nb30, Pb, K	5.11	5.11	1.57	0.56	0.21	0.10	1.95	N D	9.50	1.67	79.5	6.6	1932
1	36	None	4.84	3.84	0.86	0.29	0.12	0.12	2.60	3.80	7.83	1.85	66.8	6.2	1927
2	21	Nb72, P, K, Ca	5.82	5.82	0.89	0.45	0.13	0.06	0.89	N D	8.24	1.10	89.2	6.8	1932
2	30	Nb24, P, K, Ca	7.12	3.90	1.53	0.32	0.14	0.04	0.00	N D	5.93	1.03	100+	7.3	1932

TABLE 17—Concluded

TIER	PLOT	FERTILIZERS ALTERNATE YEARS	TOTAL Ca EX- TRACTED	Ca	Mg	K	Na	NH ₄	H TITRA- TION	H NH ₄ Ac	TOTAL CO ₂	PER CENT SATU- RATION	pH	YEAR SAMPLED
2	31	Ns48, P, K, Ca	6.70	5.23	1.51	0.37	0.12	0.07	0.00	N D	7.30	100+	7.15	1932
2	32	Ns72, P, K, Ca	6.60	4.65	1.33	0.53	0.12	0.15	0.00	N D	6.78	100+	7.00	1932
3	1	None	4.42	3.57	1.68	0.30	0.11	0.04	2.00	N D	7.70	74.0	6.53	1932
3	2	Nb24	3.40	2.68	1.14	0.25	0.11	0.04	3.44	N D	7.66	55.1	5.8	1932
3	3	P	4.49	3.64	1.14	0.14	0.11	0.02	2.70	N D	7.75	62.7	6.2	1932
3	4	K	3.64	2.99	1.39	0.68	0.14	0.06	2.10	N D	7.36	71.5	6.5	1922
3	8	None	4.24	3.74	1.33	0.23	0.12	0.06	2.10	N D	7.58	72.3	6.5	1932

Nb24, etc. refer to dried blood equal to 24 pounds of N.

Nn and Ns refer to nitrate of soda and sulfate of ammonia.

P refers to superphosphate equivalent to 48 pounds P₂O₅. Previous to 1917 dissolved bone black was used in place of superphosphate.

Pb refers to ground bone, equivalent to 48 pounds P₂O₅.

K always refers to muriate of potash equal to 100 pounds K₂O.

M6, M8, and M-10 refer to 6, 8, and 10 tons manure.

On plot 34, two tons CaCO₃ on corn and wheat.

On plot 22 and 23, two tons CaO are applied to corn only.

In both correlations, with one or two exceptions a close relationship is shown to exist. When exchange hydrogen is determined by titrating the ammonium acetate extract it is found that soils with pH values of 7.00 are about 75 per cent saturated; when, however, direct titration is resorted to, it is found that soils 100 per cent saturated have pH values very close to 7.00. The writer favors the latter method. It should be mentioned however, that the determination of exchange hydrogen by titration of the ammonium acetate extract was not performed exactly as recommended by Schollenberger. The extraction was not carried out in the absence of air, which might account for higher results with this method than with direct titration of the soil. However, the writer has generally found that normal ammonium acetate becomes more, rather than less, alkaline on exposure to the atmosphere.

SUMMARY

The effect of cropping, with its crop removals, augmented leaching, organic decay, and erosion, is brought out by comparing the unfertilized plots with the adjacent grass strips. Cultivation has resulted in a small decrease of exchangeable calcium and magnesium without an increase in exchangeable hydrogen. The quantity of exchange ammonium in the grass strips is two to three times greater than in the check plots.

Barnyard manure caused an increase in total exchange capacity, the increase being mainly due to replaceable hydrogen and magnesium. The quantity of other ions is not changed.

On those plots which have received large amounts of lime, either as burnt lime or as limestone, ever since the field experiment was begun, the soils are saturated with calcium, a large quantity of calcium is present as carbonate, and the total exchange capacity is increased. Replaceable magnesium is also higher on these plots, but the other cations are unaffected. Within a few weeks after lime is applied, whether it be CaO or CaCO₃, the pH value becomes approximately 8.3 to 8.4. Immediately after liming with burnt lime the pH value is raised considerably above these values.

The continued use of a mixture of superphosphate and muriate of potash, when compared with the check plots, has resulted in an increase in total exchange capacity. This fertilizer combination has decreased the replaceable calcium and increased the hydrogen content. Magnesium is unaffected, but potassium is decidedly increased.

Superphosphate alone caused neither increase nor decrease in calcium but did increase exchange hydrogen. This fertilizer has resulted in a diminution of magnesium and potassium which is believed to be due to larger crop removals than on the check plots. Superphosphate increases soil acidity slightly.

When compared with superphosphate, ground bone is found to increase replaceable calcium and the degree of saturation and to raise the pH value of the soil.

Dried blood has resulted in marked loss of calcium and magnesium with corresponding increase in hydrogen. The amount of bases lost and of hydrogen gained is not directly proportional to the quantity of blood used. It is concluded that when soils become depleted of active bases the stronger acids may leach out as iron or alumina salts or as free acids.

The sodium of nitrate of soda was not adsorbed, and the quantity of other bases was not altered by the use of large amounts of nitrate of soda. Hydrogen was reduced and the total exchange capacity diminished by from 2 to 3 m.e.

As a result of the use of large amounts of sulfate of ammonia over a period of 50 years there has been a marked decrease of calcium and magnesium and a small loss of potassium. Hydrogen has replaced these ions so that now the most acid plots are only 15 per cent saturated. It is noteworthy that, although this salt has reduced the quantity of three bases, Ca, Mg, and K, the ill effects are apparently overcome by lime alone. It is pointed out that under field conditions it is not possible to determine, by calculation, how much lime is needed to counteract the acidity produced by an application of sulfate of ammonia.

Muriate of potash appears to have replaced calcium by potassium. Though there has been a loss of calcium there has been no gain in hydrogen and no appreciable change in pH value.

A comparison is made between the three most acid plots on tier 1, unlimed, and the corresponding three plots on tier 2, limed in 1921. This single application has restored the calcium and magnesium contents and the yields. Replaceable hydrogen has been practically eliminated, and the soils have been brought to approximately pH 7.00. Apparently no permanent injury was inflicted upon the soil as a result of being kept in such an acid condition for so long a time.

It is concluded that when fertilizer salts are used in sufficiently large amounts and for a sufficiently long period of time, they may, in some cases, produce measurable and significant effects upon the cation exchange picture of a soil. The differences so produced may have a profound influence upon the productivity of a soil.

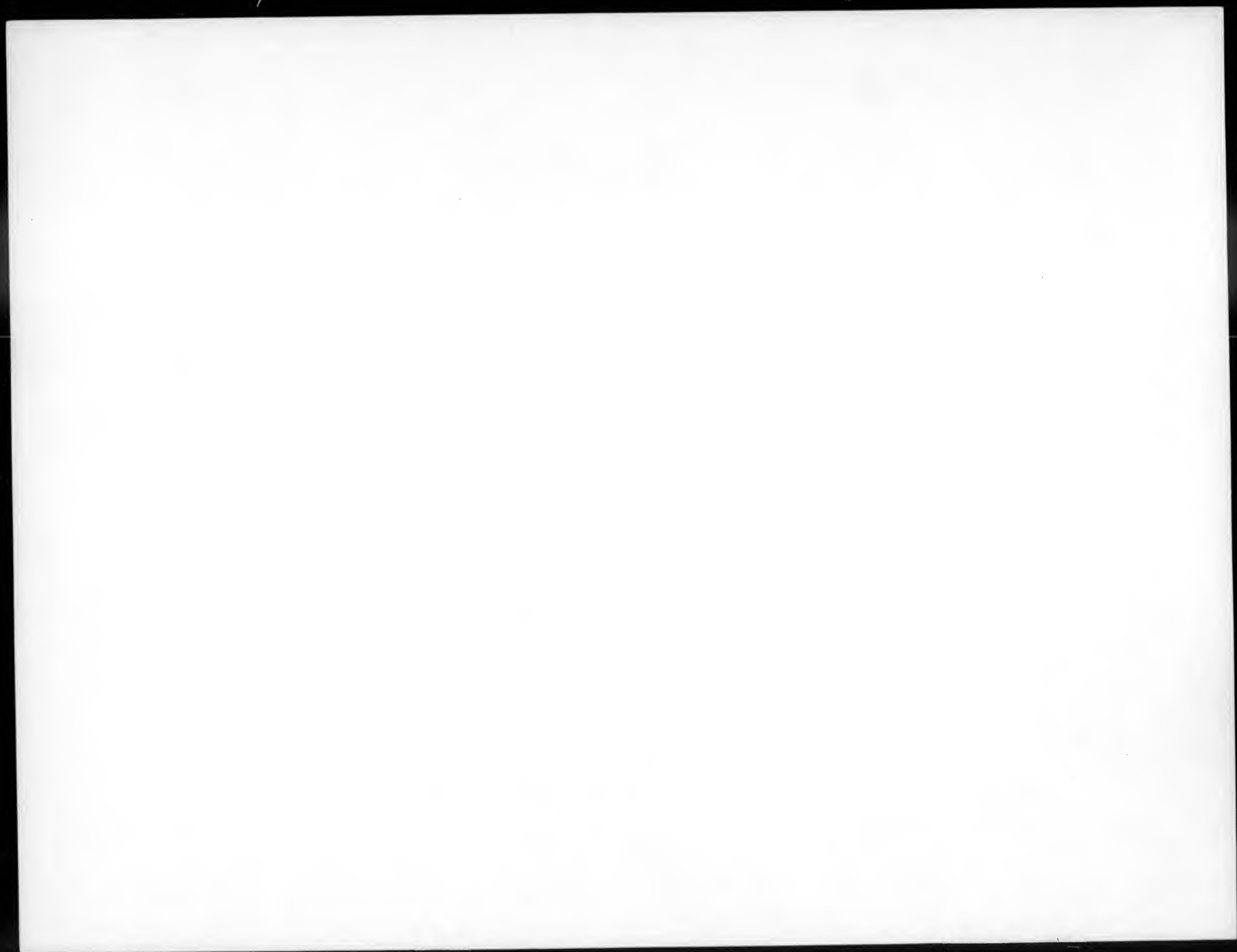
Attention is called to the fact that errors in judgment may be as serious in interpreting a field experiment that has continued for a very long period as in interpreting one that has not continued long enough.

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